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(54) **Rare earth-containing high-silica zeolite having pentasil structure and process for the same**

Seltene Erden enthaltender Zeolith mit hohem SiO₂-Gehalt und mit einer Pentasil-Struktur und Verfahren zu seiner Herstellung

Zéolithe riche en silice contenant des terres rares ayant une structure pentasil et procédé pour l'obtenir

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8488Z, page 109 ;column LEFT ;

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Description

Field of the Invention

5 The present invention relates to a crystalline aluminosilicate zeolite and process for the same, especially relates to a rare earth-containing high-silica zeolite having pentasil structure and process for the same and also the application of the high-silica zeolite in hydrocarbon conversion.

Background of the Invention

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Zeolite ZSM-5 developed by Mobil Oil Corporation (USP 3,702, 886) is a pentasil type high-silica zeolite having a pore dimension of 0.54 - 0.56 nm and a framework silica alumina ratio above 12. Based on the unique pore structure of the zeolite, it can be applied extensively as a catalytic material to various processes such as isomerization, disproportionation, catalytic cracking, catalytic dewaxing etc. However, its properties are not satisfactory, in some applications. For example, when the zeolite is used in catalytic cracking of petroleum, the enhancement of gasoline octane is accompanied by the unavoidable obvious decrease of gasoline yield (J. Oil & Gas, May 13, 1985, P. 108). When it is used as an active component of a catalyst, the remarkable framework dealumination occurs during the hydrothermal regeneration of the catalyst may cause significant loss of catalyst activity and shape selectivity (USP 4, 490, 241).

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Conventionally, the adsorptive and catalytic properties of a zeolite can be modified through ion-exchange. For example, CaA zeolite obtained by the ion-exchange of NaA zeolite with Ca^{++} possesses excellent ability for separating normal paraffin from iso-paraffin, hence can be used in the dewaxing process in petroleum refining (USP 3, 201,409). REY zeolite obtained by the ion-exchange of NaY zeolite with RE^{3+} exhibits higher activity and stability than that of NaY, hence becomes the most widely-used active component in catalytic cracking catalysts for decades (USP 3,402,976). In the case of ZSM-5 zeolite, the lower charge density within the pore channel as a consequence of the higher silica alumina ratio, the stronger hydrophobicity, and the smaller pore opening (0.54 - 0.56 nm), make it difficult to introduce trivalent state cation such as RE^{3+} into the intra-crystalline structure (P. Cho and F. G. Dwyer, ACS, Symp. Ser., 218, 59 - 78, 1983).

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Chemical Abstracts, Vol. 116, No. 2, 13 January 1992, 8488z, discloses a zeolite having a ZSM-5 X-ray diffraction pattern (i.e. of pentasil structure), smaller pore size than that of ZSM-5 and the formula

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wherein

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$$\begin{aligned} x &= 0.01-0.30, \\ y &= 0.4-0.6, \\ z &= 20-100, \end{aligned}$$

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as well as a method for the preparation thereof, in which an organic amine template and rare-earth containing faujasite seeds are used, and in which quiescent crystallization conditions are employed.

US-A- 4,175,114 describes a method for synthesizing pentasil zeolites in the presence of ZSM-5 seeds and a certain amount of NH_4OH instead of the organic amine commonly used inter alia under static conditions.

Objects of the Invention

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One object of the present invention is to provide a rare earth-containing pentasil type high-silica zeolite having narrower pore-opening for overcoming the shortcomings of the prior arts. The framework composition of the catalyst containing the zeolite of the present invention as an active component is more stable during the hydrothermal regeneration process.

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Another object of the present invention is to provide a process for synthesizing said high-silica zeolite.

A further object of the present invention is to provide catalysts containing the zeolite of the present invention as active component.

In particular, the invention is directed to preparing rare earth-containing pentasil zeolites without resorting to an organic amine template, such as used in the Chemical Abstract mentioned hereinabove.

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Summary of the invention.

The present invention therefore relates to a process for synthesizing a synthetic crystalline aluminosilicate zeolite possessing a pentasil typed structure, characterized in that said zeolite has an anhydrous chemical composition

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(based on moles of oxides) of formula:



wherein $x = 0.01-0.30$, $y = 0.4-1.0$, $z = 20-60$;
said zeolite possessing any of the X-ray diffraction patterns of Table 1.

Table 1

X - ray diffraction pattern of the zeolite of the present invention			
Zeolite of Example 1		H -type zeolite of Example 8	
d(Å)	100 I/I ₀	d(Å)	100 I/I ₀
11.17	40	11.18	37
10.01	35	10.01	40
9.76	12	9.75	10
7.45	4	7.44	3
7.08	1.5	7.09	1.5
6.71	6	6.72	3.5
6.37	8	6.37	7
6.01	11	6.00	11
5.72	10	5.71	8
5.58	10	5.58	9
5.37	3	5.38	2
5.15	3	5.14	3
5.04	5	5.05	5
4.985	8	4.983	8
4.621	6	4.620	6
4.366	10	4.369	7
4.267	13	4.265	12
4.090	5	4.085	2
4.010	9	4.010	7
3.861	100	3.856	100
3.819	74	3.817	72
3.755	41	3.752	36
3.720	49	3.719	39
3.650	28	3.652	26
3.591	7	3.593	4
3.481	9	3.479	6
3.447	13	3.447	11

and its normal hexane adsorption/cyclohexane adsorption ratio being 2-4 times higher than that of H-ZSM-5 zeolite, comprising dispersing rare earth-containing faujasite seed in a gel system comprising water glass, aluminium salt, inorganic acid and water, with oxide mole ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30-120$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2-15$, and $\text{H}_2\text{O}/\text{SiO}_2 = 20-100$, wherein the amount of the seed used should satisfy the mole ratio of RE_2O_3 (from seed) and Al_2O_3 (in said gel system) being

in the range of 0.01-0.40, and crystallizing in a still state at 130-200°C for 12-60 hours followed by filtrating, washing and drying. The high-silica zeolite of the present invention can be used as catalysts for hydrocarbon conversion in a variety of catalytic conversion processes in the field of hydrocarbon processing and petrochemical processes.

5 Detailed Description of the Invention

The method of present invention provides a rare earth-containing pentasil type crystalline aluminosilicate high-silica zeolite having an anhydrous chemical composition (based on the mole ratios of oxides) of formula:



wherein $X=0.01 - 0.30$, $y=0.4 - 1.0$, $z=20 - 60$.

It possesses a X-ray diffraction pattern listed in Table 1 and 2 - 4 times higher normal hexane/cyclohexane adsorption ratio than that of ZSM-5 zeolite.

15 The rare earth elements contained in the high-silica zeolite of the present invention originate from the rare earth-containing seeds used for synthesis. The composition of said zeolite is formed through the reaction of rare earth-containing faujasite seeds with the gel system composing of water glass, aluminium salt, inorganic acid, and water. Said rare earth - containing faujasite seed is REY, REHY, or REX, which contains 2 - 27 wt. % rare earth elements and < 7.0 wt. % sodium (both based on the weight of oxide).

20 The high-silica zeolite of the present invention having above-mentioned anhydrous composition can be converted to H-type high-silica zeolite through ammonium-exchange and calcination, which possesses a X - ray diffraction pattern listed also in Table 1.

Table 2 is a comparison of X - ray diffraction patterns between, the high-silica zeolite and H-type of said high-silica zeolite of the present invention and ZSM-5 and H-ZSM-5 zeolite of U.K. Patent No. 1, 161, 974.

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Table 2

The comparison of X - ray diffraction patterns.							
ZSM-5 (U. K. Pat. No. 1,161,974)		Zeolite of the present invention (Example 1)		HZSM-5 (U. K. Pat. No. 1,161,974)		H-zeolite of the present invention (Example 8)	
d(Å)	100I/I ₀	d(Å)	100I/I ₀	d(Å)	100I/I ₀	d(Å)	100I/I ₀
11.10	29	11.17	40	11.12	100	11.18	37
9.97	23	10.01	35	9.96	55	10.01	40
9.70	23	9.76	12	9.74	47	9.75	10
7.44	6.5	7.45	4	7.44	6.5	7.44	3
7.08	3	7.08	1.5	7.00	5	7.09	1.5
6.68	3	6.71	6	6.70	8	6.72	3.5
6.35	8	6.37	8	6.36	12	6.37	7
6.04	7	6.01	11	6.02	18	6.00	11
5.72	6	5.72	10	/	/	5.71	8
5.56	8	5.58	10	5.57	13	5.58	9
5.37	4	5.37	3	5.37	5	5.38	2
5.13	2	5.15	3	5.15	2	5.14	3
/	/	5.04	5	/	/	5.05	5
4.997	4	4.985	8	4.994	4	4.983	8
4.601	6	4.621	6	4.603	7	4.620	6
4.355	6.5	4.366	10	4.358	5	4.369	7
4.259	8	4.267	13	4.262	9	4.265	12
4.077	1.5	4.090	5	/	/	4.085	2
3.999	6.5	4.010	9	4.002	6	4.010	7
3.837	100	3.861	100	3.842	96	3.856	100
3.818	53	3.819	74	3.822	46	3.817	72
3.749	37	3.755	41	3.752	43	3.752	36
3.716	44	3.720	49	/	/	3.719	39
3.646	31	3.650	28	3.649	15	3.652	26
/	/	3.591	7	/	/	3.593	4
/	/	3.481	9	/	/	3.479	6
3.437	7	3.447	13	3.442	6	3.447	11

Table 2 indicates that the line intensities of the XRD pattern of the high-silica zeolite of the present invention are evidently different from that of ZSM-5 zeolite, and some new lines appear in the XRD pattern of the zeolite of the present invention, which do not exist in the XRD pattern of ZSM-5 zeolite. The chemical composition of the high-silica zeolite of the present invention is characterized in containing intra-crystalline trivalent rare earth cations. The pore opening of the zeolite of the present invention is narrower than that of ZSM-5 zeolite, and normal hexane/cyclohexane adsorption ratio on the zeolite of the present invention is higher than that on ZSM-5 zeolite. Table 3 is the comparison of normal hexane/cyclohexane adsorption ratio between the high-silica zeolite of the present invention and ZSM-5 zeolite.

Table 3

Example	Adsorption n-hexane*	Capacity, mg/g cyclohexane	n-hexane absorbed/cyclohexane absorbed
8	100.8	14.8	6.81
9	103.5	14.2	7.29
10	104.2	15.1	6.90
11	102.9	13.9	7.51
12	105.1	15.6	6.74
13	101.7	14.6	6.96
14	102.5	15.0	6.83
HZSM-5	112.0	52.2	1.98

* The kinetic diameter of n-hexane is 0.43 nm.

** The kinetic diameter of cyclohexane is 0.61nm.

As shown in Table 3, the normal hexane/cyclohexane adsorption ratios on the high-silica zeolite of the present invention is higher than that on ZSM-5 zeolite.

The performance characteristics of the high-silica zeolite of the present invention, such as better hydrothermal stability and catalytic activity compared to ZSM-5 zeolite, will be further described hereinafter.

The present invention also provides a process for synthesizing said high-silica zeolite, comprising dispersing homogeneously the rare earth-containing faujasite seeds into a gel system composing of water glass, aluminium salt, inorganic acid, and water, crystallizing at 130 - 200°C, preferably at 160 - 190°C, for 12 - 60 hours, preferably for 16 - 30 hours, filtrating, washing, and finally drying.

The mole composition of said gel system is as follows:

$\text{SiO}_2/\text{Al}_2\text{O}_3 = 30 - 120$

$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2 - 15$

$\text{H}_2\text{O}/\text{SiO}_2 = 20 - 100$

Said crystallization seed is REY, REHY, or REX, which contains rare earth elements 2 - 27% and sodium < 7.0% (both based on the weight of oxides). The amount of the seed used should satisfy the mole ratio of RE_2O_3 (from seed) and Al_2O_3 (in said gel system) being in the range of 0.01 - 0.40.

Said aluminium salt is $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , and aluminium salts of phosphoric acid such as AlPO_4 , $\text{Al}_2(\text{HPO}_4)_3$, or $\text{Al}(\text{H}_2\text{PO}_4)_3$, preferably AlPO_4 , most preferably AlPO_4 gel. AlPO_4 gel can be prepared as follows:

Pseudo-boehmite and aqueous phosphoric acid solution are mixed together homogeneously according to the weight ratio $\text{Al}_2\text{O}_3 : \text{H}_3\text{PO}_4 : \text{H}_2\text{O} = 1 : 1.5 - 3.0 : 5 - 15$, followed by ageing in still state at ambient temperature for more than 4 hours, preferably for more than 24 hours, to prepare AlPO_4 gel.

Said inorganic acid is phosphoric acid, sulfuric acid, hydrochloric acid, or nitric acid. The amount of the inorganic acid used should make the pH value of the system in the range of 10 - 12.

The preparation of the rare earth-containing faujasite used as seed in the present invention is as follows:

REY zeolite seed

NaY zeolite is exchanged with RECl_3 solution according to the weight ratio of zeolite (dry base): $\text{RECl}_3 : \text{H}_2\text{O} = 1 : 0.01 - 11.0 : 10 - 100$, preferably $1 : 0.1 - 0.5 : 20 - 80$, for 2.0 hours, followed by filtrating and calcining in flowing dry air or 100% steam at 400 - 600°C for 0.5 - 4.0 hours. The calcined zeolite may undergo above-mentioned exchange-calcination procedure for one more time.

REHY zeolite seed

NaY zeolite is exchanged with aqueous $(\text{NH}_4)_2\text{SO}_4$ solution according to the weight ratio of zeolite (dry base): $(\text{NH}_4)_2\text{SO}_4 : \text{H}_2\text{O} = 1 : 0.2 - 4.0 : 10 - 40$, preferably $1 : 0.8 - 2.0 : 20 - 30$, at 50 - 150°C, preferably 80 - 120°C, for 0.2

- 20 hours, followed by filtrating. Said procedure of exchange and filtration can be repeated 1 - 2 times. The filter cake is calcined in flowing dry air at 400-600°C for 0.5 - 4.0 hours. The calcined zeolite is exchanged with RECl_3 solution according to the weight ratio of zeolite (dry base) : RECl_3 : H_2O = 1 : 0.05 - 1.0 : 10 - 100, preferably 1 : 0.2 - 0.8 : 20 - 50, at 50 - 150°C, preferably 80 - 120°C, for 0.2 - 2.0 hours. After filtration, the filter cake may be calcined in flowing dry air at 400 - 600°C for 0.5 - 4.0 hours, or may not be calcined.

REX zeolite seed

NaX zeolite is exchanged with RECl_3 solution according to the weight ratio of zeolite (dry base): RECl_3 : H_2O = 1 : 0.01 - 1.0 : 10 - 100, preferably 1 : 0.1 - 1.0 : 10 - 100, preferably 1 : 0.1 - 0.6 : 20 - 60, at 50 - 150°C, preferably at 60 - 120°C, for 0.2 - 2.0 hours. After filtration, the filter cake is calcined in flowing dry air or 100% steam at 400 - 550°C for 0.5 - 4.0 hours. The above-mentioned exchange-calcination procedure may be repeated for the calcined zeolite.

As mentioned above, the high-silica zeolite of the preset invention contains rare earth elements, possesses pentasil type structure, has narrower pore opening, better activity-stability for hydrothermal treatment, and better shape selectivity, compared with ZSM-5 zeolite. After conventional NH_4^+ exchange and Na^+ washing-off, the high-silica zeolite of the present invention can be incorporated with other active components and/or matrix components such as SiO_2 , Al_2O_3 , SiO_2 - Al_2O_3 , and clays, to formulate catalysts used in various catalytic conversion processes including hydrocarbon processing and petrochemical production, such as catalytic cracking, deep catalytic cracking, catalytic dewaxing, hydrocracking, hydroisomerization, and so forth.

The present invention will be further described with reference to the following examples. However, these examples are not to be construed to limit the scope of the present invention.

Example 1

100 g (dry base) NaY zeolite having silica/alumina mole ratio of 5.0 (the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio was determined by X-ray diffraction in all examples) as dispersed in 2100g 1.5 wt. % RECl_3 (containing 49 wt. % Ce_2O_3 and 24 wt. % La_2O_3) solution. The ion-exchange proceeded at 90°C for 30 minutes with stirring. After filtration, the filter cake was calcined in flowing dry air at 550°C for 2 hours. The above-mentioned exchange-calcination procedure was repeated once more. The REY seed thus obtained had a chemical composition (wt. %) as follows:

RE_2O_3 18.2, Na_2O 1.5, Al_2O_3 19.5, and SiO_2 60.7.

The Na_2O content was determined by atomic absorption spectroscopy, while the other components were determined by X-ray fluorescence spectroscopy.

60g (dry base) pseudo-boehmite was dispersed while stirring homogeneously in 375 g 30 wt. % aqueous H_3PO_4 solution. After keeping in still state for 24 hours at ambient temperature, the AlPO_4 gel containing 13.5 wt. % Al_2O_3 was obtained, which could be diluted to any concentration when in use.

2.8g above-prepared REY seed was dispersed in 200g water glass containing 3.5 wt. % Na_2O and 11.1 wt. % SiO_2 . 54.9g AlPO_4 gel containing 1.1 wt. % Al_2O_3 was added to the above mixture while stirring. A 25 wt. % H_2SO_4 solution was used to adjust the PH of the above system making it into a gel state. The mole composition of the prepared gel was: 0.26 RE_2O_3 8.9 Na_2O Al_2O_3 60.0 SiO_2 0.98 P_2O_5 2220 H_2O (Al_2O_3 from seed was not included in the calculation, same for other examples). The prepared gel was crystallized at 180°C for 22 hours. After cooling and filtrating, the filter cake was washed with water to a neutral PH value, followed by drying at 110 - 120°C. The obtained high-silica zeolite thereof had an anhydrous chemical composition (based on the mole ratio of oxides, same for other examples) as follows:

0.9 Na_2O 0.13 RE_2O_3 Al_2O_3 31.2 SiO_2

and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 31.2.

Example 2

0.5g REY zeolite seed prepared in Example 1 was dispersed in 180 g water glass containing 3.8 wt. % Na_2O , and 11.0 wt. % SiO_2 . 38.3 g AlPO_4 gel containing 1.1 wt. % Al_2O_3 was added to the mixture while stirring. A 11.0 wt. % H_3PO_4 solution was used to adjust the PH value of the system making a gel. The mole composition of the prepared gel was:

0.07 RE_2O_3 4.05 Na_2O Al_2O_3 80.0 SiO_2 7.6 P_2O_5 3142 H_2O .

The prepared gel was crystallized at 190°C for 16 hours, followed by, filtrating, washing, and drying as described in Example 1. The obtained high-silica zeolite thereof had an anhydrous chemical composition as follows:

0.95 Na_2O 0.03 RE_2O_3 Al_2O_3 52.0 SiO_2

and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 52.0.

Example 3

REY zeolite seed was prepared according to the method described in Example 1 except that 100 g NaY zeolite having a silica/alumina mole ratio of 4.2 instead of 5.0 was used, the weight percentages of oxide components in the prepared REY seed were:

RE_2O_3 : 20.1, Na_2O : 1.4, Al_2O_3 : 21.9, and SiO_2 : 56.6.

2.5 g REY seed prepared above was dispersed in 195g water glass containing 3.7 wt. % Na_2O and 11.7 wt. % SiO_2 . 51.7 g AlPO_4 gel containing 1.5 wt. % Al_2O_3 was added to the mixture while stirring. A 23 wt. % H_3PO_4 solution was added to the system making it into gel state. The mole composition of the gel was:

0.21 RE_2O_3 3.10 Na_2O Al_2O_3 50.0 SiO_2 4.08 P_2O_5 1680 H_2O

The gel obtained was crystallized at 185°C for 20 hours, followed by filtrating, washing, and drying. The high-silica zeolite obtained thereof had a mole composition of:

0.77 Na_2O 0.14 RE_2O_3 Al_2O_3 36.3 SiO_2

and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 36.3.

Example 4

100 g NaY zeolite having a silica/alumina mole ratio of 5.0 was dispersed in 2100g 5.0 wt. % $(\text{NH}_4)_2\text{SO}_4$ solution. The ion-exchange proceeded at boiling temperature for 30 minutes. Distilled water was added during the exchange process to maintain a constant volume. After ion-exchange and filtrating, the filter cake was calcined in flowing dry air at 550°C for 2 hours. The calcined product was added to 5000g 1.0 wt. % RECl_3 solution. The ion-exchange proceeded at 90°C for 30 minutes. After filtrating, the REHY seed obtained had a weight percentage composition as follows:

RE_2O_3 10.0, Na_2O 0.6, Al_2O_3 20.5, SiO_2 68.7

3.0 g REHY seed prepared above was dispersed in 180g water glass containing 3.8 wt. % Na_2O and 11.0 wt. % SiO_2 . 42.1g AlPO_4 gel containing 0.8 wt. % Al_2O_3 was added to the mixture while stirring. A 20 wt. % HCl solution was added to adjust the pH value of the system making it into gel state. The mole composition of the gel was:

0.27 RE_2O_3 12.5 Na_2O Al_2O_3 100 SiO_2 0.97 P_2O_5 3655 H_2O .

The gel obtained was crystallized at 170°C for 30 hours, followed by filtrating, washing, and drying. The high-silica zeolite obtained thereof had a mole composition as follows:

0.86 Na_2O 0.08 RE_2O_3 Al_2O_3 39.5 SiO_2

and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 39.5.

Example 5

100 g NaX zeolite having a silica/alumina mole ratio of 2.9 was dispersed in 2500g 1.5 wt. % RECl_3 solution. The ion-exchange proceeded at 90°C for 30 minutes. After filtration, the filter cake was calcined in flowing dry air at 550°C for 2 hours. The weight percentage composition of REX seed obtained therefrom was:

RE_2O_3 18.5, Na_2O 6.0, Al_2O_3 27.9, SiO_2 47.6

1.0 g prepared above REX seed was dispersed in 180 g water glass containing 3.5 wt. % Na_2O and 11.1 wt. % SiO_2 . 42.5 g AlCl_3 solution containing 1.0 wt. % Al_2O_3 was added to the mixture while stirring. A 30 wt. % H_3PO_4 solution was used to adjust the pH value of the system making it into gel state. The mole composition of the gel was:

0.13 RE_2O_3 7.0 Na_2O Al_2O_3 80.0 SiO_2 7.2 P_2O_5 2785 H_2O .

The obtained gel was crystallized at 150°C for 45 hours, followed by filtrating and washing. The high-silica zeolite obtained thereof had a mole composition as follows:

0.84 Na_2O 0.07 RE_2O_3 Al_2O_3 42.9 SiO_2

and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 42.9.

Example 6

REX zeolite seed was prepared according to the method described in Example 5 except that the same exchange-calcination procedure was repeated once more after the filter cake was calcined in flowing dry air at 550°C for 2 hours. The weight percentage composition of REX seed obtained was:

RE_2O_3 25.0, Na_2O 1.3, Al_2O_3 26.6, SiO_2 47.0.

2.0 g prepared REX seed was dispersed in 200g water glass containing 3.7 wt. % Na_2O and 11.7 wt. % SiO_2 . 75.8g AlPO_4 gel containing 1.5 wt. % Al_2O_3 was added to the mixture while stirring. A 5.1 wt. % H_3PO_4 solution was used to adjust the pH value of the system making it into gel state. The mole composition of the gel was :

0.14 RE_2O_3 2.2 Na_2O Al_2O_3 35.0 SiO_2 2.8 P_2O_5 1580 H_2O

The gel obtained was crystallized at 195°C for 13 hours, followed by filtrating, washing, and drying. The high-silica zeolite obtained thereof had a mole composition as follows:

0.81Na₂O 0.10RE₂O₃ Al₂O₃ 24.8SiO₂
and had a SiO₂/Al₂O₃ mole ratio of 24.8.

Example 7

REX zeolite seed was prepared according to the method described in Example 5 except that the same exchange-calcination procedure was repeated once more after the filter cake was calcined in flowing 100% steam at 550°C for 2 hours. The weight percentage composition of REX seed obtained was:

RE₂O₃ 25.2, Na₂O 1.1, Al₂O₃ 25.1, SiO₂ 48.6.

15 g prepared REX seed was dispersed in 1130 g water glass containing 3.5 wt. % Na₂O and 11.1 wt. % SiO₂. 130g Al₂(SO₄)₃ solution containing 2.5 wt. % Al₂O₃ was added to the mixture while stirring. A 20 wt. % H₂SO₄ solution was used to adjust the pH value of the system making it into gel state. The mole composition of the gel was:

0.36 RE₂O₃ 9.7 Na₂O Al₂O₃ 65.6 SiO₂ 2380 H₂O.

The gel obtained was crystallized at 180°C for 20 hours, followed by filtrating, washing, and drying. The high-silica zeolite obtained thereof had a mole composition as follows:

0.77 Na₂O 0.15 RE₂O₃ Al₂O₃ 34.5 SiO₂

and had a SiO₂/Al₂O₃ mole ratio of 34.5.

Examples 8-14

The high-silica zeolites prepared in Examples 1-7 were ion-exchanged at 90°C for 1 hour, respectively, according to a weight ratio of zeolite : (NH₄)₂SO₄ : H₂O = 1 : 1 : 20. After filtration, the exchange-filtration procedure was repeated once more. The filter cake was then dried at 110-120°C, calcined at 550°C for 2 hours. The respective H-type products were thus obtained. Their adsorption properties were listed in Table 3.

Comparative Example 1

5 g ZSM-5 zeolite seed was dispersed in 1 litre water glass (specific gravity 1.3) containing 40.5 g/l Na₂O and 126.0g/l SiO₂. 71.6 g 33 wt. % ethyl amine solution and 51.0g Al₂(SO₄)₃ solution containing 7.0 wt. % Al₂O₃ were added subsequently to the mixture while stirring. A dilute H₂SO₄ was used to adjust the pH value of the system making it into gel state. The mole composition of the gel was:

7.9 Na₂O Al₂O₃ 60.0SiO₂ 15.0 C₂H₅NH₂ 2500H₂O

The gel obtained was crystallized at 140°C for 50 hours, followed by cooling, filtrating, washing, and drying. The anhydrous mole composition of the prepared ZSM-5 zeolite was:

1.03 Na₂O Al₂O₃ 45.8 SiO₂

The prepared ZSM-5 zeolite had a X-ray diffraction pattern listed in Table 2, and a SiO₂/Al₂O₃ mole ratio of 45.8.

Comparative Example 2

The corresponding H-ZSM-5 zeolite was prepared from ZSM-5 zeolite of comparative Example 1 according to the method described in Examples 8-14 and a weight ratio of zeolite : (NH₄)₂SO₄ : H₂O = 1 : 1 : 20. Its adsorption property was listed in Table 3.

Example 15 Stability Test

The zeolite prepared in Example 11 was ion-exchanged twice with a 5 wt. % (NH₄)₂SO₄ aqueous solution at 90°C for 1 hour (each time) according to a weight ratio of zeolite (dry base) : (NH₄)₂SO₄ = 1 : 1. The ion-exchange was followed by filtrating, washing, drying at 110-120°C, and calcining at 550°C for 2 hours. The H-type zeolite obtained thereof containing 1.9 wt. % RE₂O₃ and 0.03 wt. % Na₂O.

The washed and dried samples were treated in 100% steam at 800°C for 1, 2, 4 and 8 hours respectively. Relative crystallinity retention of the treated samples were determined by X-ray diffraction, wherein the relative crystallinity retention was defined as the ratio of the intensity of the diffraction line at the position of Cuk 23.0 of the treated sample and the original sample. The results were listed in Table 4.

Table 4

Treating time (hr.)	Crystallinity retention(%)
1	90.1
2	86.0
4	85.1
8	85.0

After treated in 100% steam at 800°C for different time length, the H-type zeolite samples were tested in a pulse reactor at 480°C using n-C₁₄ alkane as feedstock to evaluate cracking activity, wherein activity=(1-fraction of unconverted n-C₁₄) X 100%. The results were listed in Table 5.

Table 5

Treating time (hr.)	n-C ₁₄ cracking activity(%)
0	100
1	94
2	85
4	80
8	70

Comparative Example 3

ZSM-5 zeolite was treated according to the method of Example 5 to obtain H-ZSM-5 containing 0.01 wt. % Na₂O.

The washed and dried H-ZSM-5 samples were treated in 100% steam at 800°C for 1, 2, 4, and 8 hours respectively. The relative crystallinity retention of the treated samples were listed in Table 6.

Table 6

Treating time (hr.)	Crystallinity retention(%)
1	94.0
2	94.2
4	94.0
8	92.8

After treated in 100% steam at 800°C for different time length, the H-ZSM-5 samples were tested in a pulse reactor at 480°C and atmospheric pressure using n-C₁₄ as feedstock to evaluate cracking action. The results were listed in Table 7.

Table 7

Treating time (hr.)	n-C ₁₄ cracking activity(%)
0	100
1	67
2	62
4	45
8	30

The results in Tables 4-7 show that, after treated under rather severe conditions, the relative crystallinity retention of the high-silica zeolite of the invention can maintain a level above 85%. As far as the figures of the crystallinity retention are concerned, the hydrothermal structure-stability of the zeolite of the invention seems slightly lower than that of H-ZSM-5. However, the hydrothermal activity-stability of the zeolite of the invention is significantly higher than that of H-ZSM-5.

Example 16 Activity for deep catalytic cracking

5.3 kg aluminium sulfate solution containing 7.0 wt. % Al_2O_3 was dispersed homogeneously in 20 kg water glass (modulus 3.2) containing 5.5 wt. % SiO_2 by stirring. A 10 wt. % ammonia water was used to adjust the PH value to 6.5 - 7.5. A silica-alumina gel containing 25 wt. % Al_2O_3 was obtained.

0.145 kg high-silica zeolite prepared according to the method described in Example 1 was ground and dispersed in the above-prepared silica-alumina gel. After homogenizing and spray-drying, the product was twice exchanged with $(\text{NH}_4)_2\text{SO}_4$ followed by washing and drying. The catalyst for deep catalytic cracking obtained contained 9 wt. % high-silica zeolite of the invention and less than 0.1 wt. % Na_2O .

The prepared catalyst was treated in 100% steam at 800 for 4 hours, and then tested in a pilot fixed-fluidized bed reactor under reaction condition: 580°C, cat/oil ratio 5.0 and WHSV 1.0 h^{-1} . The feedstock used was a VGO having a distillation range of 197 - 479°C and Conradson carbon 0.06 wt. %. The results of the deep catalytic cracking test were listed in Table 8.

Table 8

Conversion, wt. %	84.56
Product yield, wt. %	
Cracking gas	50.65
H ₂	0.38
CH ₄	3.18
C ₂ H ₆	1.61
C ₂ H ₄	4.20
C ₃ H ₈	3.69
C ₃ H ₆	17.96
i-C ₄ ⁰	3.66
n-C ₄ ⁰	1.28
C ₄ ⁻¹	2.41
i-C ₄ ⁻	6.36
t-C ₄ ⁻²	3.45
cis-C ₄ ⁻²	2.47
Gasoline(C ₅ - 221°C)	26.22
LCO(221 - 330°C)	9.78
Heavy oil(> 330°C)	5.66
Coke	7.69
C ₂ ⁻ + C ₃ ⁻ + C ₄ ⁻	36.85
ΣC ₄ ⁻	14.69

Comparative Example 4

The catalyst was prepared according to the method described in Example 16 except that 0.323 kg ZSM-5 zeolite was used for the preparation of catalyst instead of the high-silica zeolite prepared in Example 2 of the present invention. The deep catalytic cracking catalyst obtained thereof contained 18 wt. % ZSM-5 zeolite. The same reaction condition and feedstock as used in Example 16 were used herein for the deep catalytic cracking test. The results were listed in Table 9.

Table 9

Conversion, wt. %	84.77
Product yield, wt. %	
Cracking gas	48.30
H ₂	0.37
CH ₄	3.10
C ₂ H ₆	1.59
C ₂ H ₄	3.68
C ₃ H ₈	3.26
C ₃ H ₆	17.04
i-C ₄ ⁰	3.29
n-C ₄ ⁰	1.13
C ₄ ⁻ -1	2.40
i-C ₄ ⁻	6.44
t-C ₄ ⁻ -2	3.50
cis-C ₄ ⁻ -2	2.50
Gasoline(C ₅ - 221°C)	29.04
LCO(221 - 330°C)	9.96
Heavy oil(> 330°C)	5.27
Coke	7.43
C ₂ ⁻ + C ₃ ⁻ + C ₄ ⁻	35.56
C ₄ ⁻	14.84

The data listed in table 8 and 9 show that although the content of the high-silica zeolite of the present invention in the deep catalytic cracking catalyst is only half of the content of ZSM- 5 zeolite in the comparative catalyst, the conversion levels in both catalysts are nearly the same and the olefin yield on the former catalyst is even slightly higher.

Example 17

The silica-alumina gel containing 25 wt. % Al₂O₃ prepared in Example 16 was also used in this example.

0.368 kg high-silica zeolite prepared according to the process described in Example 1 was ground and dispersed in the above-mentioned silica-alumina gel. After homogenizing and spray-drying, the product was ion-exchanged twice with (NH₄)₂ SO₄ followed by washing and drying. The octane-enhancement promoter for catalytic cracking obtained contained 20 wt. % high-silica zeolite of the invention and less than 0. 1 wt. % Na₂O.

The promoter obtained was treated in 100% steam at 760 °C for 4 hours. After treatment, it was dispersed, according to a ratio of 1:99, to an industrially balanced Y-7 catalyst(REY zeolite based cracking catalyst, produced by the catalyst factory of Qilu Petrochemical Corp., SINOPEC). The well-mixed catalyst was tested in a fixed-fluidized bed reactor under reaction conditions of 500°C, cat./oil ratio 3.8, and WHSV 8.0 h⁻¹, using VGO (same as the VGO used in Example 16) as feedstock. The results were listed in Table 10.

Table 10

	Balanced Y-7 catalyst	Balanced Y-7 catalyst mixed with the promoter of the present invention
Conversion, wt. %	62.26	68.55
Product yield, wt. %		
H ₂ - C ₂	1.63	1.44
C ₃ - C ₄	14.34	16.45
Gasoline(C ₅ - 221°C)	46.85	47.31
LCO(221 -330°C)	18.90	18.42
Heavy oil (>330°C)	14.84	13.03
Coke	3.44	3.35
Gasoline RON(clear)	89.2	91.0
MON(clear)	78.6	80.2
Octane-barrel	4179.0	4305.2

25 Comparative Example 5

The octane-enhancement promoter for catalytic cracking was prepared according to the process described in Example 17 except that 0.368 kg ZSM-5 zeolite was used instead of high-silica zeolite prepared in Example 1 of the present invention. The content of ZSM-5 in the prepared promoter was 20 wt. %.

The prepared octane-enhancement promoter was treated in 100% steam at 760°C for 4 hours. The treated sample was dispersed, according to a ratio of 1:99, to an industrially balanced Y-7 catalyst. The well-mixed catalyst was tested for its activity in catalytic cracking reaction according to the process described in Example 17. The results were listed in Table 11.

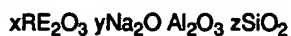
Table 11

	Balanced Y-7 catalyst	Balanced Y-7 catalyst mixed with ZSM-5 pro- moter
Conversion, wt. %	62.26	66.56
Product yield, wt. %		
H ₂ - C ₂	1.63	1.43
C ₃ - C ₄	14.34	15.57
Gasoline(C ₅ - 221°C)	46.85	46.20
LCO(221 - 330°C)	18.90	18.50
Heavy oil (>330°C)	14.84	14.94
Coke	3.44	3.38
Gasoline RON(clear)	89.2	90.3
MON(clear)	78.6	79.5
Octane-barrel	4179.0	4171.9

The data listed in Table 10 and 11 show that the octane-enhancement promoter containing high-silica zeolite of the present invention has higher gasoline octane-barrel and hydrothermal activity-stability.

Claims

1. A process for synthesizing a synthetic crystalline aluminosilicate zeolite possessing a pentasil type structure, characterized in that said zeolite has an anhydrous chemical composition (based on moles of oxides) of formula:



wherein $x = 0.01-0.30$, $y = 0.4-1.0$, $z = 20-60$;

said zeolite possessing any of the following X-ray diffraction patterns:

Zeolite or		H-type zeolite	
d(Å)	100 I/I ₀	d(Å)	100 I/I ₀
11.17	40	11.18	37
10.01	35	10.01	40
9.76	12	9.75	10
7.45	4	7.44	3
7.08	1.5	7.09	1.5
6.71	6	6.72	3.5
6.37	8	6.37	7
6.01	11	6.00	11
5.72	10	5.71	8
5.58	10	5.58	9
5.37	3	5.38	2
5.15	3	5.14	3
5.04	5	5.05	5
4.985	8	4.983	8
4.621	6	4.620	6
4.366	10	4.369	7
4.267	13	4.265	12
4.090	5	4.085	2
4.010	9	4.010	7
3.861	100	3.856	100
3.819	74	3.817	72
3.755	41	3.752	36
3.720	49	3.719	39
3.650	28	3.652	26
3.591	7	3.593	4
3.481	9	3.479	6
3.447	13	3.447	11

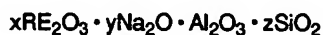
and its normal hexane adsorption/cyclohexane adsorption ratio being 2-4 times higher than that of H-ZSM-5 zeolite, comprising dispersing rare earth-containing faujasite seed in a gel system comprising water glass, aluminium salt, inorganic acid and water, with oxide mole ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30-120$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2-15$, and $\text{H}_2\text{O}/\text{SiO}_2 = 20-100$, wherein the amount of the seed used should satisfy the mole ratio of RE_2O_3 (from seed) and Al_2O_3 (in said gel system) being in the range of 0.01-0.40, and crystallizing in a still state at 130-200°C for 12-60 hours followed

by filtrating, washing and drying.

2. A process according to claim 1, wherein said seed is REY, REHY, or REX, containing rare earth element 2-27 % and sodium < 7.0% (both based on the weight of oxides).
- 5 3. A process according to claim 1, wherein said aluminium salt is $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , AlPO_4 , $\text{Al}_2(\text{HPO}_4)_3$, or $\text{Al}(\text{H}_2\text{PO}_4)_3$.
4. A process according to claim 3, wherein said aluminium salt is AlPO_4 .
- 10 5. A process according to claim 4, wherein said aluminium salt is AlPO_4 gel.
6. A process according to claim 1, wherein said inorganic acid is phosphoric acid, sulfuric acid, hydrochloric acid, or nitric acid.
- 15 7. A process according to claim 1, wherein the amount of said inorganic acid used should make the pH-value of the system in the range of 10-12.
8. A process according to claim 1, wherein said still state crystallization proceeds at 160-190°C for 16-30 hours.
- 20 9. Hydrocarbon conversion catalyst containing zeolite made by the process of claim 1

Patentansprüche

1. Verfahren zur Synthese eines synthetischen kristallinen Altkminosilikatzeoliths, der eine Struktur vom Pentasiltyp aufweist, dadurch gekennzeichnet, daß der Zeolith eine wasserfreie chemische Zusammensetzung (bezogen auf Mole Oxid) der Formel aufweist:
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- 30 in der $x = 0,01 - 0,30$, $y = 0,4 - 1,0$, $z = 20 - 60$ ist;
wobei der Zeolith eines der folgenden Röntgenbeugungsmuster aufweist:

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Zeolith oder		Zeolith vom H-Typ	
d(Å)	100 I/I ₀	d(Å)	100 I/I ₀
11,17	40	11,18	37
10,01	35	10,01	40
9,76	12	9,75	10
7,45	4	7,44	3
7,08	1,5	7,09	1,5
6,71	6	6,72	3,5
6,37	8	6,37	7
6,01	11	6,00	11
5,72	10	5,71	8
5,58	10	5,58	9
5,37	3	5,38	2
5,15	3	5,14	3
5,04	5	5,05	5
4,985	8	4,983	8
4,621	6	4,620	6
4,366	10	4,369	7
4,267	13	4,265	12
4,090	5	4,085	2
4,010	9	4,010	7
3,861	100	3,856	100
3,819	74	3,817	72
3,755	41	3,752	36
3,720	49	3,719	39
3,650	28	3,652	26
3,591	7	3,593	4
3,481	9	3,479	6
3,447	13	3,447	11

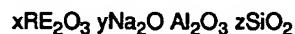
und sein normales Verhältnis der Hexanadsorption/Cyclohexanadsorption zwei- bis viermal höher ist als das von H-ZSM-5-Zeolith, umfassend das Dispergieren von Seltene Erden enthaltenden Faujasitkeimen in einem Gelsystem, umfassend Wasserglas, Aluminiumsalz, anorganische Säure und Wasser, mit einem Oxid-Molverhältnis von $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30-120$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2-15$, und $\text{H}_2\text{O}/\text{SiO}_2 = 20-100$, wobei die Menge der verwendeten Keime dem Molverhältnis von RE_2O_3 (aus Keimen) und Al_2O_3 (in dem Gelsystem) das Bereich von 0,01-0,40 genügen sollte, und 12-60 Stunden lang Kristallisieren in einem ruhenden Zustand bei 130-200°C und anschließendes Filtrieren, Waschen und Trocknen.

- Verfahren nach Anspruch 1, wobei der Keim REY, REHY oder REX ist, der 2-27% Seltenerdelement und < 7,0% Natrium (beide bezogen auf das Gewicht der Oxide) enthält.
- Verfahren nach Anspruch 1, wobei das Aluminiumsalz $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , AlPO_4 , $\text{Al}_2(\text{HPO}_4)_3$, oder $\text{Al}(\text{H}_2\text{PO}_4)_3$ ist.
- Verfahren nach Anspruch 3, wobei das Aluminiumsalz AlPO_4 ist.

5. Verfahren nach Anspruch 4, wobei das Aluminiumsalz AlPO_4 -Gel ist.
6. Verfahren nach Anspruch 1, wobei die anorganische Säure Phosphorsäure, Schwefelsäure, Chlorwasserstoffsäure oder Salpetersäure ist.
7. Verfahren nach Anspruch 1, wobei die Menge der verwendeten anorganischen Säure den pH-Wert des Systems in den Bereich von 10-12 bringen sollte.
8. Verfahren nach Anspruch 1, wobei die Kristallisation in dem ruhenden Zustand 16-30 Stunden lang bei 160-190°C fortschreitet.
9. Katalysator zur Konversion von Kohlenwasserstoff, der durch das Verfahren von Anspruch 1 hergestellten Zeolith enthält.

Revendications

1. Procédé de synthèse d'une zéolite aluminosilicate cristalline synthétique à structure de type pentasil, caractérisé en ce que la zéolite présente une composition chimique anhydre (sur la base des rapports molaires en oxydes) de formule :



où $x = 0,01-0,30$, $y = 0,4-1,0$, $z = 20-60$;

ladite zéolite produisant l'un des spectres de diffraction aux rayons X suivants :

X

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Zéolite ou		Zéolite type H	
d(Å)	100I/I ₀	d(Å)	100I/I ₀
11,17	40	11,18	37
10,01	35	10,01	40
9,76	12	9,75	10
7,45	4	7,44	3
7,08	1,5	7,09	1,5
6,71	6	6,72	3,5
6,37	8	6,37	7
6,01	11	6,00	11
5,72	10	5,71	8
5,58	10	5,58	9
5,37	3	5,38	2
5,15	3	5,14	3
5,04	5	5,05	5
4,985	8	4,983	8
4,621	6	4,620	6
4,366	10	4,369	7
4,267	13	4,265	12
4,090	5	4,085	2
4,010	9	4,010	7
3,861	100	3,856	100
3,819	74	3,817	72
3,755	41	3,752	36
3,720	49	3,719	39
3,650	28	3,652	26
3,591	7	3,593	4
3,481	9	3,479	6
3,447	13	3,447	11

et son rapport habituel adsorption d'hexane/adsorption de cyclohexane étant deux à quatre fois plus élevé que celui d'une zéolite H-25M-5, cette procédé comprenant la dispersion d'un germe de faujasite contenant des terres rares dans un gel constitué de verre soluble, de sel d'aluminium, d'acide inorganique et d'eau, dans un rapport molaire en oxydes $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30-120$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2-15$ et $\text{H}_2\text{O}/\text{SiO}_2 = 20-100$, dans lequel la quantité de germe utilisée doit correspondre au rapport molaire de RE_2O_3 (provenant du germe) et de Al_2O_3 (dans ledit gel) compris dans l'intervalle 0,01-0,40, et la cristallisation à l'état de repos à 130-200°C pendant 12-60 heures, suivie d'une filtration, d'un lavage et d'un séchage.

2. Procédé selon la revendication 1, dans lequel le germe est du REY, du REHY ou du REX contenant de 2 à 27 % de terres rares et du sodium en quantité inférieure à 7,0 % (chacun sur la base du poids en oxydes).
3. Procédé selon la revendication 1, dans lequel le sel d'aluminium est du $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , AlPO_4 , $\text{Al}_2(\text{HPO}_4)_3$ ou $\text{Al}(\text{H}_2\text{PO}_4)_3$.

4. Procédé selon la revendication 3, dans lequel le sel d'aluminium est du AlPO_4 .
5. Procédé selon la revendication 4, dans lequel le sel d'aluminium est un gel de AlPO_4 .
- 5 6. Procédé selon la revendication 1, dans lequel l'acide inorganique est de l'acide phosphorique, de l'acide sulfurique, de l'acide hydrochlorique ou de l'acide nitrique.
7. Procédé selon la revendication 1, dans lequel la quantité d'acide inorganique utilisée doit porter le pH de l'ensemble à une valeur comprise dans l'intervalle 10-12.
- 10 8. Procédé selon la revendication 1, dans lequel la cristallisation à l'état de repos s'effectue à 160-190°C pendant 16-30 heures.
9. Catalyseur de conversion d'hydrocarbure contenant la zéolite obtenue par mise en oeuvre du procédé selon la
15 revendication 1.

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